Modeling of N2O Emissions in a Full-Scale Activated Sludge Sequencing Batch Reactor

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Abstract. Nitrous oxide (N2O) is a greenhouse gas with a signiﬁcant global warming potential. A dynamic model was developed to estimate the N2O pro- duction and emission in a full-scale sequencing batch reactor (SBR) municipal wastewater treatment plant (WWTP). Based on the Activated Sludge Model 1 (ASM1), the model considered all known biological and abiotic N2O production pathways along with the application of a ‘stripping effectivity’ (SE) coefﬁcient for reflecting the non-ideality of the stripping model. N2O data of two different cycles (types B and C) were used for the model calibration. Cycle B involved the alternation amongst aerated and non-aerated phases, whereas cycle C included a unique long aerobic phase. Optimizing the dissolved oxygen (DO) and SE parameters for both cycles provided a good ﬁt of the model (DO = 1.6 mg L−1 and SE = 0.11 for cycle B, and DO = 1.66 mg L−1 and SE = 0.11 for cycle C). In both cases, N2O emission peaks were related to high nitrite concentration in the liquid phase. Nitriﬁer denitriﬁcation was identiﬁed as the predominant biological pathway for N2O generation. Although SBR oper- ation occurred at similar DO and SE values for both cycles, the emission factor was signiﬁcantly different; 0.8% for cycle B and 1.5% for cycle C, indicating the impact of cycle conﬁguration on the N2O emission. Thus, optimized SBR operation is essential in order to achieve a low overall carbon footprint through the avoidance of high N2O emissions and energy requirements.

Keywords: N2O emissions · Sequencing batch reactor · Full-scale modeling

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# 1 Introduction

Nitrous oxide (N2O) is a greenhouse gas (GHG) with a global warming potential 265 times higher than carbon dioxide in a 100-year period (IPCC [2013](#_bookmark13)). During wastewater treatment, N2O production and emission is mostly observed during the biological nutrient removal (Pan et al. [2016](#_bookmark13)). With such a signiﬁcant greenhouse effect, the development of mathematical models estimating N2O dynamics emerges as an effective way to study the effect of operational conditions to decrease the carbon footprint in WWTPs. The implementation of these models will enable the establishment of miti- gation strategies and, subsequently, optimal plant design and process control (Mannina et al. [2016](#_bookmark13); Pocquet et al. [2016](#_bookmark13); Massara et al. in press).

Three different biological pathways have been suggested for N2O production during the biological nitrogen (N) removal in wastewater treatment plants (WWTPs): nitriﬁer denitriﬁcation, incomplete hydroxylamine (NH2OH) oxidation and hetero- trophic denitriﬁcation. The ﬁrst two occur through the activity of Ammonia Oxidizing

Table 1 List of the 20 processes considered in our ASM-type model for 4-step nitriﬁcation-denitriﬁcation combined with a 2-pathway model for N2O production by AOB and two abiotic processes.

|  |  |  |
| --- | --- | --- |
| Process Number | Process | |
| 1 | Hydrolysis | Aerobic Hydrolysis |
| 2 | Anoxic Hydrolysis (NO—3 ! NO—2 ) |
| 3 | Anoxic Hydrolysis (NO—2 ! N2) |
| 4 | Anaerobic Hydrolysis |
| 5 | Heterotrophic organisms | Aerobic Growth on Ss |
| 6 | Anoxic Growth of Heterotrophs on Ss (NO—3 ! NO—2 ) |
| 7 | Anoxic Growth of Heterotrophs on Ss (NO—2 ! NO) |
| 8 | Anoxic Growth of Heterotrophs on Ss (NO ! N2O) |
| 9 | Anoxic Growth of Heterotrophs on Ss (N2O ! N2) |
| 10 | Lysis |
| 11 | Nitrifying organisms | NH3 oxidation to NH2OH with oxygen consumption |
| 12 | NH2OH oxidation to NO coupled with oxygen reduction (AOB growth here) |
| 13 | NO oxidation to NO—2 coupled with oxygen reduction |
| 14 | NO reduction to N2O coupled with the NH2OH oxidation to NO—2 (N2O from NH2OH oxidation pathway) |
| 15 | HNO2 reduction to N2O coupled with NH2OH oxidation to NO—2 (N2O from nitriﬁer denitriﬁcation pathway) |
| 16 | Aerobic Growth of NOB |
| 17 | Lysis of AOB |
| 18 | Lysis of NOB |
| 19 | Abiotic N2O production | NH2OH decomposition to N2O |
| 20 | N-nitrosation of NH2OH (HNO2 as nitrosating agent) |

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Bacteria (AOB) (Wunderlin et al. [2012](#_bookmark14)). It is common practice to apply the IWA Activated Sludge Models (ASM) (Henze et al. [2000](#_bookmark9)) for the description of biological chemical oxygen demand (COD) and nutrient removal in WWTPs. However, the original ASM models take no account of the N2O production and quantiﬁcation. Hence, the aims of this work were: (i) to create an ASM-type model integrating the N2O dynamics for a full-scale municipal sequencing batch reactor (SBR) plant, and

(ii) calibrate the developed model with real N2O emission data from the previous relevant study of Rodriguez-Caballero et al. ([2015](#_bookmark13)) (Table [1](#_bookmark0)).

# 2 Materials and Methods

The model presented in this paper was based on the ASM1 (Henze et al. [2000](#_bookmark9)) and was modiﬁed to include phosphate consumption by nitriﬁers and heterotrophs. Afterwards, it was coupled with the two-pathway model of Pocquet et al. ([2016](#_bookmark13)) for N2O pro- duction by AOB. Moreover, the heterotrophic denitriﬁcation steps were imported from Hiatt and Grady ([2008](#_bookmark10)). Furthermore, recent studies have revealed that abiotic N2O production pathways can have a non-negligible contribution to the emissions during wastewater treatment (Harper et al. [2015](#_bookmark8); Soler-Jofra et al. [2016](#_bookmark13)). For that reason, abiotic N2O production (i.e. NH2OH decomposition to N2O, and N-nitrosation of NH2OH with nitrous acid as nitrosating agent) (Domingo-Félez and Smets [2016](#_bookmark4)) was also considered. Thus, the ﬁnal model incorporated all the currently known pathways for N2O production.

The kinetic model was developed in MATLAB and implemented for an existing full-scale SBR performing COD and N removal in the municipal WWTP of La Roca del Valles (Barcelona, Spain) (48,000 population equivalents). Rodriguez-Caballero et al. ([2015](#_bookmark13)) examined different operational cycles to evaluate the effects on N2O production. They continuously monitored both gaseous and dissolved N2O using a gas analyzer and a microsensor, respectively, for 33 days between February and March 2014 corresponding to a total number of 143 cycles. Those measurements served for the calibration of the model presented in the current study.

Two different cycle types (type B and C) applied by Rodriguez-Caballero et al. ([2015](#_bookmark13)) for the same influent are presented in this abstract. They both began with a 10-min lag phase during which the mixed liquor was stirred before feeding started. Cycle B involved the alternation amongst two aerated (13–40 min) and two non-aerated phases (\*25 min). The reaction phase for Cycle C included the sequence of two shorter non-aerated phases (\*25 min) with a long aerated one (66 min) between them. Feeding was continuous. Details on the operational parameters and influent characteristics used in this work can be found in Rodriguez-Caballero et al. ([2015](#_bookmark13)).

N2O stripping was modeled by using the dissolved N2O concentration and the volumetric mass transfer coefﬁcient (*kLa*) for N2O. We also included a ‘stripping effectivity’ (SE) coefﬁcient expressing the non-ideality of this typical simpliﬁed model.

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# 3 Results and Discussion

The total N2O emission (in g N-N2O d−1) for a cycle was an additional simulated variable. The evolution of this variable in time was used for calculating the instanta- neous N2O emission. The results are given in Figs. [1](#_bookmark1) and [2](#_bookmark2) for cycle B and cycle C, respectively.

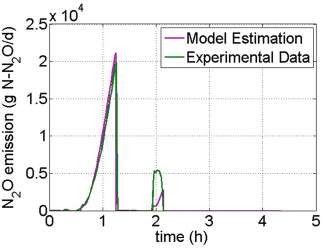


Fig. 1. *Optimized Cycle type B:* The N2O instantaneous emission estimated by the model compared to the experimental data. Optimized DO setpoint during the aerated phases = 1.6 mg L−1.

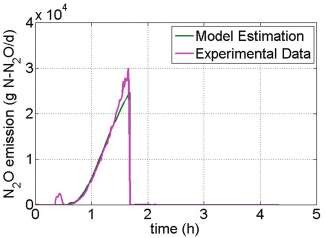


Fig. 2. *Optimized Cycle type C:* The N2O instantaneous emission estimated by the model compared to the experimental data. Optimized DO setpoint during the aerated phases = 1.66 mg L−1.

N2O emissions are expected to be negligible in the non-aerated phases due to the negligible stripping (Ahn et al. [2010](#_bookmark5)). In accordance with this idea, both the experi- mental data and our model linked the emissions with air flow or, equivalently, with the aerated phases. Within the attempt to calibrate the model, the SE parameter was ﬁrstly evaluated. For both cycle types, a rather satisfactory ﬁtting to the experimental N2O emission occurred under the same *kLa* modelling approach and SE value. It was noted that a SE equal to 0.11 contributed to a quite successful description of the experimental data in both cases, thus suggesting a clear influence of the stripping modeling on the ﬁnal results.

According to the Global Water Research Coalition, the nitriﬁcation-related microbial routes (i.e. the two AOB pathways) are considered as major hotspots for N2O emissions in full-scale domestic WWTPs (GWRC et al. [2011](#_bookmark6)). During nitriﬁca- tion, insufﬁcient aeration has an inhibitory effect (Kampschreur et al. [2009](#_bookmark11)), and can therefore lead to increased emissions through the AOB pathways. After the SE study, we explored the DO setpoint during the aerobic phases of each cycle as an important operational parameter. The results after the DO setpoint and SE optimization for cycles B and C are shown in Figs. [1](#_bookmark1) and [2](#_bookmark2), respectively. First, it can be seen that the simulation results are ﬁtted well on the experimental ones. However, this version of the model with default kinetic parameters was unable to precisely capture the emission peak at the beginning of the 2nd aerated phase of Cycle B (Fig. [1](#_bookmark1)); especially the part of

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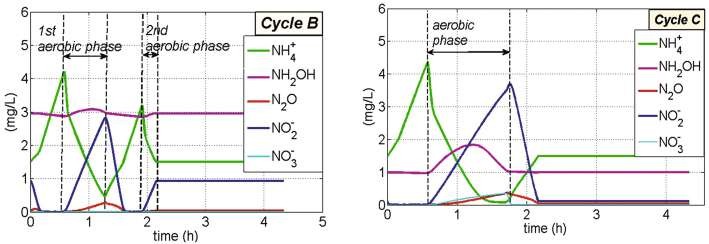


Fig. 3. *Optimized Cycles type B & C:* The evolution of the NH4+, NH2OH, N2O, NO—2 and NO—3

concentrations.

the emissions noted at the very beginning of the peak. It can be hypothesized that these emissions were rapidly recorded as a result of the stripping of the N2O produced during the previous anoxic phase. This effect could be related to a N2O denitriﬁcation rate during the anoxic phase lower than the value predicted by the model, which could lead to a higher ﬁnal N2O concentration at the end of the anoxic phase that would be stripped at the beginning of the aerobic phase. This divergence was not observed in cycle C because in this case only one aerobic phase existed. Speciﬁc experiments to evaluate N2O denitriﬁcation rate would help to improve the model ﬁtting. Secondly, we received the following output of the optimization process: optimal DO = 1.6 mg L−1 and SE = 0.11 (cycle B), optimal DO = 1.66 mg L−1 and SE = 0.11 (cycle C). Both cycle types were applied for the same influent. The optimal ﬁt occurred at similar DO setpoint and SE. However, the emission factor differed signiﬁcantly, being 0.8% for cycle B and 1.5% for cycle C. This is probably attributed to the long aerated phase of cycle C which can be connected with the higher N2O emissions. As shown in Fig. [3](#_bookmark3) for both cycles, the N2O concentration peaks coincided with the nitrite (NO2−) peaks in the liquid phase. This was observed for both the long aerobic phase of cycle C as well as for the 1st aerobic phase of cycle B; as mentioned above, the 2nd aerobic phase of cycle B was less successfully depicted in our simulations. Consequently, it can be deduced that nitriﬁer denitriﬁcation was the predominant AOB pathway for N2O generation. The optimal ﬁt was obtained for a rather low DO setpoint (1.6 mg L−1 for cycle B and

1.66 mg L−1 for cycle C). This observation is in agreement with past studies regarding

the AOB pathways relative contribution; compared to incomplete NH2OH oxidation, nitriﬁer denitriﬁcation has been suggested as increasingly contributing with the DO decrease (Anderson et al. [1993](#_bookmark7); Sutka et al. [2006](#_bookmark13); Kampschreur et al. [2008](#_bookmark12)).

# 4 Conclusions

It can be concluded that the cycle conﬁguration influences the emission magnitude. Long aerobic phases can increase the plant’s carbon footprint due to the following:

(i) higher energy requirements, (ii) higher N2O production through the

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nitriﬁcation-related pathways, and (iii) subsequent N2O emission because of stripping. In this frame, process optimization is important. Optimal SBR operation includes the application of an optimal DO setpoint during aerobic phases of medium length. Under optimized SBR operation, satisfying nitriﬁcation along with moderate N2O emissions and reasonable energy requirements are more likely to be achieved. In that sense, the implementation of cycles with multiple (shorter) aerated phases (e.g. cycle B in this work) instead of cycle conﬁgurations with few and relatively long aeration periods (e.g. cycle C in this work) seems more suitable.

This work will hopefully constitute a flexible model for the prediction and miti- gation of N2O emissions in full-scale SBR WWTPs with the added value of easily adapting to different cycle types.

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